A Differential Refractometer*

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The design and performance of an absolute deviation type of differential refractometer is described. The apparatus comprises mercury and sodium lamps, monochromatic filters, slit, differential cell, projection lens, and micrometer microscope, all accurately aligned on an optical bench. The cell is square with a thin partition separating solution and solvent, such that the angle of incidence is about 69° on the interface. The cell and its holder, in a jacketed housing, can be turned through 180° in order to interchange solvent and solution and approximately double the deviation. By ray tracing it is shown that the distance between the slit images in the eyepiece field, Δd, is accurately proportional to the difference in refractive index, Δn, of solution and solvent, and that the factor of proportionality can be evaluated from accurately measurable geometrical quantities: the cell partition angle, the virtual distance from slit to cell center, and the magnification of the system up to the field of the micrometer eyepiece. The range of the instrument is approximately 0.01 unit and the limiting sensitivity about 3×10^{-6} unit of refractive index difference. The accuracy in determination of Δn is about 0.5 percent. The instrument is useful for determination of small differences in refractive index or concentration, and for determination of refractive index increments needed in the light-scattering method of evaluating high molecular weights.

I. INTRODUCTION

THE measurement of small differences in the refractive index of liquids has found increasing use in recent years, particularly in the determination of high molecular weights by the method of Debye,[1] in following fractionation by distillation or adsorption,[2–5] in determining concentrations of colorless solutes in dilute solutions,[6,7] and in studies of sedimentation equilibrium.[8,9] A difference in refractive index can be measured with a precision of about one unit in the fifth decimal place by means of the Pulfrich, high precision Abbé, or dipping refractometers,[10] but requires temperature control to 0.02°C or better. This quantity can be measured more readily and with higher accuracy in a differential instrument, which may be based on interferometry or on the direct determination of a deviation. The former, typified by the Rayleigh-Haber-Löwe interferometer[10] for liquids, is capable of an accuracy of about one unit in the seventh decimal place of difference in refractive index. The deviation or image displacement type of instrument, which is now in more common use, is usually capable of an accuracy of several units in the sixth decimal place. This is adequate for most of the applications named above. Differential instruments are superior to conventional refractometers not only in accuracy but also in simplicity of temperature control. Ambient temperature need not be closely controlled since the temperature coefficient of the difference in refractive index between a solution and its solvent is much smaller than that for the refractive index of solution or solvent alone. It is essential, however, that solution and solvent in the differential cell have the same temperature to 0.01° or better.

A number of optical arrangements for differential refractometers of the deviation type were described by Kessler[11] for use with both liquids and gases. The basic instrument comprises a slit source of monochromatic light, a double prism cell mounted on a spectrometer table, and a micrometer ocular or divided circle for determining deviations. The differential refractometer to be described in the present paper is a modification of this basic instrument, differing principally in the optical system and method of evaluating absolute differences in refractive index from its geometry. Other modifications, requiring calibration with solutions of known refractive index, have been described: that of Rau and Roseveare[6] with a double slit, double prism cell, and a thin wedge moving along the optic axis to compensate for deviation when solvent is replaced by solution in one compartment of the differential cell; a similar arrangement by Dutton,[3] with a single slit and monochromatic light; that of P. P. Debye,[12] with a double prism cell and a micrometer microscope for determining deviations; that of Hadow *et al.*;[13] and those of Stamm,[14] Thomas *et al.*,[5] and Zaukelies and Frost,[4] with double prism cells and photoelectric indication or recording of deviations. The present absolute instrument is an improved form of that originally described[15]

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[1] P. Debye, J. Appl. Phys. 15, 338 (1944).
[2] S. Claesson, Arkiv Kemi, Mineral. Geol. 23A, No. 1, 1 (1946).
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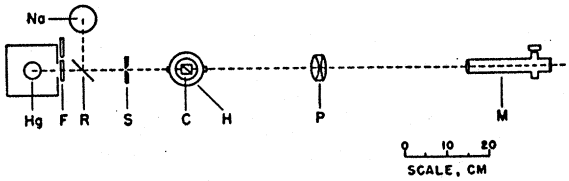

FIG. 1. Diagrammatic sketch of optical system of differential refractometer. Hg, mercury lamp in housing; *F*, monochromatic filters; *R*, semi-transparent mirror for viewing sodium lamp, Na; *S*, spectrometer slit; *C*, differential cell; *H*, jacketed cell housing; *P*, projector lens; *M*, micrometer microscope.

and was developed primarily for the evaluation of refractive increments in the determination of high molecular weights.[16]

II. DESCRIPTION OF THE INSTRUMENT

A diagrammatic sketch of the optical system of the differential refractometer is shown in Fig. 1. It comprises essentially a lamp housing containing a Type *AH*-3 mercury lamp and monochromatic filters, previously described;[16] a permanently mounted semi-transparent mirror which permits viewing either the mercury lamp or a sodium lamp, the latter not attached to the optical bench; a spectrometer slit; a differential cell of the double prism type mounted in a jacketed housing; and a projector lens ($f/4.5$, $f=164$ mm) for imaging the slit in the focal plane of the objective ($2.8\times$, $f=40$ mm) of a microscope fitted with a filar micrometer eyepiece ($12.5\times$) having a 10 mm fixed scale and a drum divided to 0.01 mm. All parts are carefully aligned on an optical bench.

The differential cell is a sinter-fused optical cell 15 mm square inside with plane parallel windows, a removable cover, and a thin (1.12 mm) diagonal glass partition which divides the cell into two compartments, one for solvent and one for solution. The cell is mounted (Fig. 2) in a double-walled housing adapted for circulation of constant temperature water and provided with a plastic lid and two ports for passage of the light beam. The cell holder inside the housing can be rotated about a vertical axis through 180° by means of a handle projecting from the fixed housing. The handle is stopped by adjustable Allen-head screws. The cell is clamped symmetrically in its holder by set screws so that the axis of rotation passes through the center of the cell, as tested by means of a depth gauge inserted in one port of the cell housing against the cell face for 0° and 180° settings of the cell.

The mountings for the lamp, slit, lens, and microscope are provided with lateral and height adjustments which can be securely locked. The apparatus is properly aligned when: (1) light passes centrally through the slit, cell housing, and along the axis of the microscope, without and with the lenses and with the cell (filled with a solvent) in the path of the beam; (2) the axis of rotation of the cell passes through the center of the cell; (3) the light beam is incident normally on the cell face for both 0° and 180° positions; (4) with the cell filled with water, the slit image falls near the center of the micrometer eyepiece scale, and there is no appreciable displacement of the slit image for 0° and 180° settings of the cell; (5) with a test solution (e.g., 0.4 M potassium chloride in distilled water) in one compartment and solvent in the other compartment of the cell, the slit images for 0° and 180° positions of the cell are of approximately equal brightness, and show minimum lateral shift of each slit image on focusing in and out; and (6) the distance between slit images on interchanging solution and solvent in the compartments of the cell is the same, within experimental error, as the displacement observed on rotating the cell through 180°. All adjustments are securely locked when this alignment is attained.

With the arrangement proposed, deviations are approximately doubled by rotation of the cell, and determination of zero position by readings on solvent need be made at only infrequent intervals. The procedure for determination of a difference in refractive index follows. The two cell compartments are filled with one milliliter each of solution and solvent, and about 10 minutes is allowed for attaining temperature equilibrium. With the cell in the 0° position (solution toward slit) the scale reading d_1 of the slit image is determined by carefully focusing the microscope and centering the cross-hair on the fine slit image. The determination is repeated about five times, displacing the cross-hair and focusing adjustment each time. The cell is then turned through 180° and the new position, d_2, of the slit image determined in a similar way. Both compartments are then filled with solvent, and the slit image positions d_{01} and d_{02} for the solvent determined in the same way as above. It is necessary to identify one compartment as the "solution compartment," since

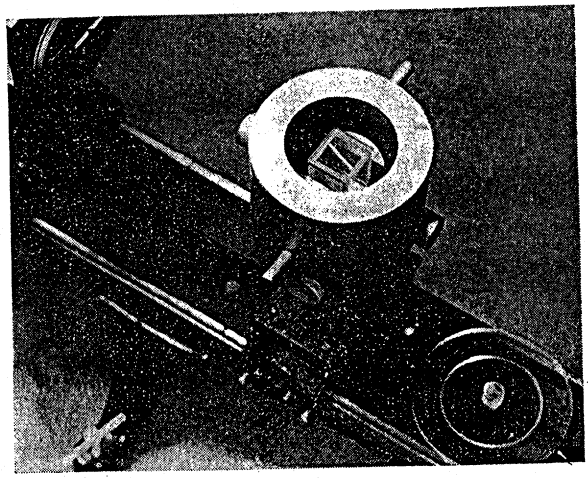

FIG. 2. Photograph of differential cell in jacketed housing. The spectrometer slit and optical bench are partly shown.

[16] Brice, Halwer, and Speiser, J. Opt. Soc. Am. 40, 768 (1950).

d_{01} is the reading obtained when this compartment is toward the slit. The value of $d_{01}-d_{02}$ may be positive or negative and will differ somewhat for different solvents. The total displacement for a given solution is:

$$\Delta d=(d_1-d_2)-(d_{01}-d_{02}). \tag{1}$$

It will be shown that the difference in refractive index between solution and solvent is strictly proportional to Δd:

$$\Delta n=k\Delta d, \tag{2}$$

and that k can be evaluated either geometrically or by means of solutions of known refractive index.

III. CALIBRATION FROM GEOMETRY

It can be shown by tracing the central ray through the optical system that the distance between the deviated slit images in the eyepiece field, Δd, is proportional to the difference in refractive index, Δn, between solution and solvent, and that the factor of proportionality can be evaluated from accurately measureable geometrical quantities: the partition angle of the cell, the distance from slit to cell center, and the magnification up to the field of the micrometer eyepiece.

In Fig. 3 light from the slit O is incident normally on the cell face at A, passes through the cell window and solvent, is incident at angle i on the thin partition, and undergoes deviations as shown on passing into the solution, the second glass window at D, and into air at E, with a final angle of refraction r. Applying Snell's law to the refractions at C, D, and E:

$$n_0 \sin i=n \sin r_1, \tag{3}$$

$$n \sin(i-r_1)=n_w \sin r_2=\sin r. \tag{4}$$

But the angles $i-r_1$ and r are very small (less than 0.026 radian in the present apparatus), and hence:

$$n(i-r_1)=r. \tag{5}$$

Solving for r_1 and substituting in Eq. (3)

$$n_0 \sin i=n \sin(i-r/n). \tag{6}$$

It follows from Eq. (6) that

$$n-n_0=r \cot i+r^2/2n. \tag{7}$$

If solution and solvent now be interchanged (or the cell be rotated through 180° through a vertical axis at C), the ray passes through solution first and is deviated downward after passing through the partition. The final angle of refraction is r'. An analysis similar to the above leads to the expression:

$$n-n_0=r' \cot i-r'^2/2n_0. \tag{8}$$

The second power terms of Eqs. (7) and (8) are not negligible compared with the first power terms. However, on adding Eqs. (7) and (8), it can be shown‡ that $r^2/2n-r'^2/2n_0$ is small compared with $(r+r')\cot i$, and hence, to a close approximation:

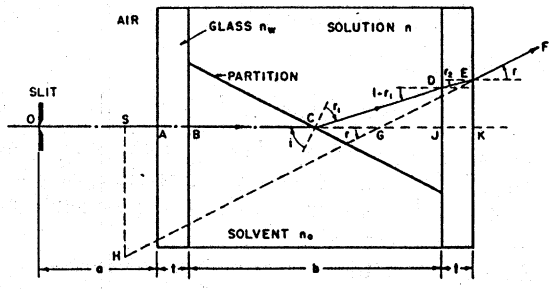

FIG. 3. Path of central ray OABCDEF through differential cell with thin partition (diagrammatic plan). The final angle of deviation is r, and the virtual image of the slit is at H (with deviations exaggerated); n_0, n, and n_w are the refractive indices of solvent, solution, and glass windows, respectively.

$$n-n_0=\tfrac{1}{2}(r+r')\cot i. \tag{9}$$

The angles r and r' can be evaluated approximately from the geometry (Fig. 3).

$$r=SH/SG=(d_0-d_2)/mSG, \tag{10}$$

where SH is the virtual displacement of the slit from the optic axis; d_2 is the scale reading for the slit image in the eyepiece field when solvent and solution are placed as in the diagram; d_0 is the scale reading for the undeviated slit image when solvent is in both compartments of the cell; and m is the magnification of the system up to the eyepiece field.

$$SG=OG-OS=a+t+b/2+CG-OS. \tag{11}$$

$$CG=CK-GK=b/2+t-KE/r. \tag{12}$$

$$KE=JD+LE=(b/2)(i-r_1)+r_2 t. \tag{13}$$

Using Eq. (5) and the fact that $r=n_w r_2$,

$$KE=(b/2)(r/n)+tr/n_w. \tag{14}$$

Hence

$$CG=(b/2)(n-1)/n+t(n_w-1)/n_w. \tag{15}$$

The distance OS is the virtual displacement of the slit along the optic axis, and is found from simple optics by considering each portion of the cell (solvent, solution, windows) as plane parallel plates passing a slightly diverging beam originating at O:

$$OS=(b/2)(n_0-1)/n_0+(b/2)(n-1)/n+2t(n_w-1)/n_w. \tag{16}$$

Substituting Eqs. (15) and (16) in Eq. (11):

$$SG=a+b/2n_0+t/n_w, \tag{17}$$

‡ This may be illustrated by a numerical example, using an 0.8 M solution of potassium chloride and distilled water, for which $n-n_0=0.007725$. A scale reading with the present apparatus, for which $i=69.69°$, approximately 80 percent full scale was obtained. The calculated values corresponding to Eqs. (7), (8), and (9) were: $r\cot i+r^2/2n=0.007570+0.000156=0.007726$; $r'\cot i-r'^2/2n_0=0.007896-0.000171=0.007725$; and $\frac{1}{2}(r+r')\cot i=0.007733$. The latter result differs from $n-n_0$ by 0.1 percent.

and

$$r=(d_0-d_2)/m(a+b/2n_0+t/n_w). \quad (18)$$

By a similar analysis

$$r'=(d_1-d_0)/m'(a+b/2n+t/n_w), \quad (19)$$

where d_1 is the eyepiece scale reading for the slit image when solvent and solution are interchanged (or the cell rotated through 180°); and m' is the magnification up to the eyepiece field.

Refocusing of the microscope is required in determining d_1 and d_2, indicating a difference in the longitudinal as well as the lateral positions of the primary images formed by the projection lens. The magnification m increases as r increases, while m' decreases as r' increases in magnitude. The magnification m_0, with solvent in both cell compartments, is however experimentally equal to the mean of m and m'. For example, for a 0.6 M solution of potassium chloride compared with distilled water: $m=1.430$, $m'=1.400$, and $m_0=1.418$.

Eqs. (18) and (19) may now be added, replacing n by n_0 in Eq. (19), since the difference $n-n_0$ is always small, and replacing $(d_0-d_2)/m+(d_1-d_0)/m'$ by $(d_1-d_2)/m_0$:

$$r+r'=(d_1-d_2)/m_0(a+b/2n_0+t/n_w). \quad (20)$$

Substituting this result in Eq. (9), to a close approximation:

$$n-n_0=(d_1-d_2)(\cot i)/2m_0(a+b/2n_0+t/n_w), \quad (21)$$

or

$$\Delta n=k\Delta d, \quad (22)$$

where

$$k=(\cot i)/2m_0(a+b/2n_0+t/n_w). \quad (23)$$

Numerical values for the constants of Eq. (22) for the present apparatus are assembled in Table I.

The quantities b, t, and $\sin i$ were measured with a comparator; and a with a high precision caliper. The magnification was determined with an estimated accuracy of ±0.002 by opening the slit to various widths from 1 to 3.5 mm and reading the positions of the slit-jaw images on the scale of the micrometer microscope, with solvent in both compartments of the cell. Slit scale readings for various openings had been corrected by previous measurements with the slit on the stage of the comparator. The magnification is slightly dependent on wavelength. The constant k is slightly dependent on solvent, but the small difference shown (water and benzene) is hardly significant.

The various positions of the optical elements, the cell angle, and other constants were chosen, after a number of preliminary experiments, to be nearly optimum in respect to the production of good slit images and high precision. A final minor adjustment was made to effect a value of k near 0.001 for convenience.

TABLE I. Calibration of differential refractometer.

Quantity	Symbol	436 mμ	546 mμ	589 mμ
Cell partition angle	i	69.69°	···	···
	$\cot i$	0.3700	···	···
Slit to cell face, mm	a	122.1	···	···
Cell length inside, mm	b	15.0	···	···
Window thickness, mm	t	2.2	···	···
Refractive index, glass	n_w	1.52	···	···
Magnification	m_0	1.409	1.418	1.418
Constant (for $n_0=1.33$)	$k\cdot10^6$	1016	1010	1010
(for $n_0=1.51$)	···	1011	1005	1005

IV. RESULTS

The accuracy of the instrument was tested by comparing results for the difference in refractive index between potassium chloride solutions and distilled water as determined with the differential refractometer, and with a dipping refractometer, with results calculated from the data of Kruis[17] obtained with an interferometric refractometer (Table II). Each determination for the differential refractometer is the average of ten pairs of readings for the slit image positions. Each determination for the dipping refractometer is based on alternate sets of six readings each on solvent and solution. All data were corrected to a temperature of 25°C. Separate experiments with the differential refractometer at temperatures ranging from 20° to 30°C indicated that Δn for KCl solutions decreases by 0.20 percent for each degree rise in temperature. The data of Table II are in close agreement. Values of $\Delta n/c$ are seen to be somewhat dependent on concentration.

Sucrose solutions are well suited for the calibration and testing of differential refractometers since reliable data for their refractive indices are readily available,[18] very pure sucrose is readily obtainable, and since $\Delta n/c$ is independent of concentration over a wide range. Data for Δn and $\Delta n/c$ for sucrose solutions, as determined by the differential refractometer and by calculation from the literature, are presented in Table III.

TABLE II. Comparison of results for the difference in refractive index between KCl solutions and distilled water at 25.0°C and for wavelength 589 mμ.

Concentration g/ml	Differential refractometer r[b]	$\Delta n\cdot10^6$	$\Delta n/c$	Other data (D—Dipping refractometer, K—Interferometric, Kruis[a])	r[b]	$\Delta n\cdot10^6$	$\Delta n/c$	Difference, percent
0.01491	3	1997	0.1339	D	6	1995	0.1338	0.1
				K		2004	0.1344	−0.4
0.02982	3	3946	0.1323	D	12	3955	0.1326	−0.2
				K		3960	0.1328	−0.4
0.04474	3	5865	0.1311	D	11	5856	0.1309	0.2
				K		5883	0.1315	−0.3
0.05965	1	7725	0.1295	D	5	7746	0.1299	−0.3
				K		7766	0.1302	−0.5

[a] Interpolated from data of Kruis, reference 17, 25.00°C, 587.56 mμ.
[b] Number of determinations.

[17] A. Kruis, Z. physik Chem. 34B, 13 (1936).

[18] F. J. Bates and Associates, Natl. Bur. Standards (U. S.), Circ. C440 (May 1, 1942). See also C. A. Browne and F. W. Zerban, *Physical and Chemical Methods of Sugar Analysis* (John Wiley and Sons, Inc., New York, 1941), third edition, Table 6.

TABLE III. Comparison of difference in refractive index between sucrose solutions and distilled water, as determined by the differential refractometer and as calculated from reference 18, for 589 mμ and 20°C.

Concentration Percent by weight	Concentration c g/ml	Differential refractometer Δn	Differential refractometer $\Delta n/c$	Calc from reference 18 Δn	Calc from reference 18 $\Delta n/c$	Percent difference
1.209	0.01212	0.001742	0.1437	0.00175	0.1444	−0.5
2.020	0.02032	0.002909	0.1432	0.00292	0.1437	−0.4
3.000	0.03030	0.004344	0.1434	0.00434	0.1432	0.1
3.998	0.04054	0.005826	0.1437	0.00581	0.1433	0.3
4.989	0.05078	0.007310	0.1440	0.00728	0.1434	0.4
			av 0.1436		0.1436	

It is concluded from the data of Tables II and III that values of Δn can be determined by this differential refractometer with an accuracy of about 0.5 percent, and that the instrument scale is accurately linear in units of Δn as stated by Eq. (2). The standard error of a determination (10 pairs of scale readings) was estimated as $\sigma = 2.9 \times 10^{-6}$ unit of refractive index difference. This value serves as an index of the limiting sensitivity of the instrument.

The specific refractive increment, $\Delta n/c$, is an optical constant required in the light-scattering method of determination of molecular weights. This quantity is characteristic of a substance dissolved in a given solvent and is ordinarily independent of concentration for dilute solutions. Data are presented in Table IV for specific refractive increments of a number of systems, determined in this laboratory by means of the differential refractometer with light of wavelengths usually used for light-scattering studies. No evidence was found for dependence on concentration in the range studied for these substances. The accuracy of the $\Delta n/c$ values is estimated at ±1 percent.

Absolute refractive indices of liquids and solutions can be determined with the differential refractometer to the fifth or sixth decimal place if suitable reference liquids of known refractive index are available. Such determinations are particularly satisfactory with dilute water solutions using the excellent data of Tilton[19] and Tilton and Taylor[20] for the refractive index of water at different temperatures and wavelengths. The range of the instrument is, however, limited to about 0.01 unit of refractive index difference.

Tests performed with potassium chloride solutions in water, and with polystyrene solutions in methyl ethyl ketone, showed that with the cell lid and cell-housing lid in place no detectable change in observed values of Δd occurred over a period of two hours. With highly volatile solvents such as neohexane, however, significant drift of Δd with time was noted. This is because of a transfer of liquid from one cell compartment to the other. Errors in such cases were minimized by lifting the lid slightly above the cell body with aluminum foil spacers, operating below room temperature, and making readings without unnecessary delay.

[19] L. W. Tilton, J. Research Natl. Bur. Standards 17, 639 (1936).
[20] L. W. Tilton and J. K. Taylor, J. Research Natl. Bur. Standards 20, 419 (1938).

TABLE IV. Specific refractive increments for various solute-solvent systems determined with the differential refractometer. Units of concentration for $\Delta n/c$ are grams per ml of solution.

Substance	Solvent	Approx concentration %	$\Delta n/c$ 436 mμ	$\Delta n/c$ 546 mμ
Polystyrene	Methyl ethyl ketone	1–2	0.231	0.220[a]
Polyethylacrylate	Acetone	1	0.109	0.106[b]
Polyvinyl palmitate	Neohexane	1	0.122	0.120[b]
Polyvinyl laurate	Neohexane	1	0.118	0.114[b]
Amylopectin	Water	1–2	0.156	0.154[c]
Sucrose octaacetate	Methanol	1–5	0.1165	0.114[a]
β-Lactoglobulin	0.1 M NaCl, pH 5.2	1–2	0.189	0.182[d]
Bovine serum albumin	0.1 M NaCl, pH 5.2	1–2	0.192	0.185[d]
Ovalbumin	0.1 M NaCl, pH 4.8	1	0.188	0.182[d]
Lysozyme	0.1 M NaCl, pH 6.2	1	0.196	0.189[d]

[a] Brice, Halwer, and Speiser, J. Opt. Soc. Am. 40, 768 (1950).
[b] J. E. Hansen, this laboratory.
[c] L. P. Witnauer, this laboratory.
[d] Halwer, Nutting, and Brice, J. Am. Chem. Soc. 73, 2786 (1951).

The finite thickness of the cell partition was neglected in the derivation of Eq. (23). More detailed calculations and experimental tests indicated that this was not an appreciable source of error. With different solvents in the cell, small lateral shifts of the emergent beam will occur (with benzene the shift is 0.0 mm, with water 0.5 mm for the present apparatus). No evidence was found, however, for appreciable errors in alignment or in results for Δn because of this effect.

The differential refractometer described has the advantages of simplicity, relative freedom from difficulties of temperature control, high precision, sensitivity, and accuracy. It has the disadvantage of a moving part which may be a source of trouble in maintaining high accuracy. Occasional checking with a 4 percent sucrose test solution has been found advisable. Reliance on geometrical calibration requires careful and critical initial alignment and a differential cell with window surfaces plane and parallel to a high degree. Two independent instruments with different constants, however, were found to give results of comparable accuracy.

V. ACKNOWLEDGMENTS

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